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In re application of: Jinliang QIAO, et al
Application No.: 10/049,233 Group No.: 1711
Filed: July 25, 2002 Examiner: Michael J. Feely
For: FULLY CURED THERMOPLASTIC ELASTOMER, PROCESS FOR ITS MANUFACTURE AND APPLICATIONS THEREOF

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**English Tranglation of priority Document CN 00109220.0A**

Title: A fully vulcanized thermoplastic elastomer, and the process of preparation thereof



## Abstract

The present invention provides a fully vulcanized thermoplastic elastomer comprising a rubber phase with particle size ≤ 1 μ, and the process of preparation thereof. Fully vulcanized powdery rubber with particle size ≤ 1 μ is blended with plastic by conventional method for blending rubbers and plastics, and thus obtaining a fully vulcanized thermoplastic elastomer, which comprises a rubber phase with a small particle size and shows high tensile strength and high elongation at break, good appearance and good processibility.

**What we claim is:**

1. A fully vulcanized thermoplastic elastomer, characterized in that the average particle size of the rubber phase of said fully vulcanized thermoplastic elastomer is $\leqslant 1\ \mu$, and the volume ratio of rubber phase to plastic is 30:70 to 75:25.

2. A fully vulcanized thermoplastic elastomer according to claim 1, characterized in that the average particle size of the rubber phase of said fully vulcanized thermoplastic elastomer is $\leqslant 0.5\ \mu$.

3. The fully vulcanized thermoplastic elastomer according to claim 1, characterized in that the volume ratio of rubber phase to plastic is 50:50 to 75:25.

4. The fully vulcanized thermoplastic elastomer according to claim 1, characterized in that the gel content of said rubber phase is $\geqslant 60\%$ by weight.

5. The fully vulcanized thermoplastic elastomer according to claim 1, characterized in that the gel content of said rubber phase is $\geqslant 75\%$ by weight.

6. The fully vulcanized thermoplastic elastomer according to claim 1, characterized in that the plastic matrix of said fully vulcanized thermoplastic elastomer comprises at least one polymer or copolymer thereof selected from the group consisting of polyamide, polypropylene, polyethylene, polyvinyl chloride, polyurethane, epoxy resin, polyester, polycarbonate, polyoxymethylene, polystyrene, polyphenylene oxide,

polyphenylene sulfide, polyimide, and polysulfone.

7. The fully vulcanized thermoplastic elastomer according to claim 1, characterized in that the rubber phase of said fully vulcanized thermoplastic elastomer comprises at least one rubber selected from the group consisting of natural rubber, styrene-butadiene rubber, carboxylated styrene-butadiene rubber, nitrile rubber, carboxylated nitrile rubber, polybutadiene rubber, chloroprene rubber, silicone rubber, and acrylic rubber.

8. A process for preparing a fully vulcanized thermoplastic elastomer according to any of claims 1 to 7, characterized in that said fully vulcanized thermoplastic elastomer is preparing by blending fully vulcanized powdery rubber having average particle size of $\leqslant 1\ \mu$ with plastic by using a rubber/plastic blending equipment, and the volume ratio of fully vulcanized powdery rubber to the plastic is 30:70 to 75:25.

9. The process according to claim 8, characterized in that the average particle size of the fully vulcanized powdery rubber is $\leqslant 0.5\ \mu$.

10. The process according to claim 8, characterized in that said fully vulcanized powdery rubber comprises at least one rubber selected from the group consisting of fully vulcanized powdery natural rubber, fully vulcanized powdery styrene-butadiene rubber, fully vulcanized powdery carboxylated styrene-butadiene rubber, fully vulcanized powdery nitrile rubber, fully vulcanized powdery carboxylated nitrile rubber, fully vulcanized powdery polybutadiene rubber, fully vulcanized powdery chloroprene rubber, fully vulcanized powdery silicone rubber, and fully vulcanized powdery acrylic rubber.

11. The process according to claim 8, characterized in that the fully vulcanized powdery rubber in the form of dry cross-linked powder or wet cross-linked emulsion is blended with the plastic.

# A fully vulcanized thermoplastic elastomer, and the process of preparation thereof

The present invention relates to a thermoplastic elastomer, more particularly, to a fully vulcanized thermoplastic elastomer obtained by blending method, a process for preparation thereof.

Fully vulcanized thermoplastic elastomer, which is prepared by the process of mechanically blending elastomer with rigid plastics under certain conditions, is one kind of new materials that have been developed since 1980s. Such thermoplastic elastomer has the features of both plastics and rubbers, i.e., it shows high elasticity of rubbers at normal temperature, and can be plasticized and molded at high temperature too. In morphology of the fully vulcanized thermoplastic elastomer, the fully crosslinked rubber phase is ispersed into the plastic matrix. Due to the crosslinking of rubber phase, the strength, elasticity, thermal resistance and compression set resistance of the fully vulcanized thermoplastic elastomer are substantially improved as compared with the un-crosslinked thermoplastic elastomer. Furthermore, the chemical resistance and processing stability are greatly improved, and the properties of the materials are widely adjustable due to the wider range of rubber/plastic blending ratio.

The fully vulcanized thermoplastic elastomers obtained by dynamic vulcanization method are known in the art, for example, are described in the literatures: "Development of fully vulcanized EPDM/PP thermoplastic elastomer", *China Synthetic Rubber Industry*, No. 5, P361-364 (1986); "Development of fully cured thermoplastic elastomer of polyolefin", *Chemical Industry and Engineering Progress*, No. 5, P16-19 (1987);

*Mechanical modification of elastomer*, editor Zu Yujun, Beijing Science and Technology Press, P335-395(1992). The term "dynamic vulcanization" used herein refers to a process of vulcanization by means of cross-linking agent and intense shear stress when blending rubbers and plastics, the cruxes of which are that the mixing should not be stopped until the vulcanization is finished and there should be sufficient amount of curing agent to ensure the full vulcanization of rubber phase.

Since the full vulcanization of rubber phase in the conventional dynamic vulcanization method was carried out during blending, the requirements of cross-linking agent, blending temperature, shear rate, blending time and collaboration therebetween is rather strict, additionally, special blending equipment is required. Therefore, the conventional method has defects of higher production cost, complex procedure, incontrollable average particle size of rubber phase and crosslinking degree, hardly to prepare fully vulcanized thermoplastic elastomer of saturated rubber (e.g. acrylic rubber and silicon rubber), and higher requirement for equipment. In respect of fully vulcanized thermoplastic elastomer, its physical properties are greatly influenced by the particle size of the rubber phase, the smaller particle size of the rubber phase, the higher tensile strength and breaking elongation of the material, and the better processability of the material. The particle size of the rubber phase of the fully vulcanized thermoplastic elastomer obtained by dynamic vulcanization is mainly dependent upon the balance between the shear rate and the speed of chemical cross-linking reaction, and thus it is difficult to obtain small particle. For example, the average particle size of rubber phase of fully vulcanized thermoplastic elastomer obtained by dynamic vulcanization is 1μ-2μ, as described by Coran A.Y. et al, *Rubb. Chem. Technol.* 53(1), 141(1980).

One object of the present invention is to provide a fully vulcanized thermoplastic elastomer, wherein the rubber phase has a particle size of $\leqslant 1\mu$.

Another object of the present invention is to provide a process for preparing said fully vulcanized thermoplastic elastomer. Being a simple procedure, said process uses general rubber/plastic blending equipment, and can well control the particle size and particle size distribution of the rubber phase as well as its cross-linking degree.

The fully vulcanized thermoplastic elastomer of the present invention is prepared as follows.

In the fully vulcanized thermoplastic elastomer of the present invention, the average particle size of the dispersed phase, i.e. rubber phase, is $\leqslant 1\ \mu$, preferably $\leqslant 0.5\ \mu$, and the volume ratio of the rubber phase to the plastic matrix is 30:70 to 75:25, preferably 50:50 to 75:25, and the gel content of said rubber phase is $\geqslant$ 60%, preferably $\geqslant$ 75%.

The plastic matrix of said fully vulcanized thermoplastic elastomer comprises at least one polymer or copolymer thereof selected from the group consisting of polyamide, polypropylene, polyethylene, polyvinyl chloride, polyurethane, epoxy resin, polyester, polycarbonate, polyoxymethylene, polystyrene, polyphenylene oxide, polyphenylene sulfide, polyimide, polysulfone and the like. The rubber phase of the fully vulcanized thermoplastic elastomer comprises at least on rubber selected from the group consisting of natural rubber, styrene-butadiene rubber, carboxylated styrene-butadiene rubber, nitrile rubber, carboxylated nitrile rubber, polybutadiene rubber, chloroprene rubber, silicone rubber, and acrylic rubber

etc.

The process used for preparing the fully vulcanized thermoplastic elastomer of the present invention comprises: blending the fully vulcanized powdery rubber having average particle size of $\leqslant$ 1 μ with the plastic, and then pelleting the obtained mixture to form the fully vulcanized thermoplastic elastomer by using a conventional rubber/plastic blending equipment. The average particle size of the fully vulcanized powdery rubber used therein is preferably $\leqslant$ 0.5μ. The volume ratio of the fully vulcanized powdery rubber to the plastic is preferably 30:70 to 75:25, more preferably 50:50 to 75:25. For blending, the powdery rubber and the plastic can be mixed and extruded at one time; alternatively, a part of powdery rubber and plastic can be first blended to form an agglomerate particle, and then blended and extruded with the rest powdery rubber.

When preparing the present fully vulcanized thermoplastic elastomer, the plastic matrix comprises at least one polymer or copolymer thereof selected from the group consisting of polyamide, polypropylene, polyethylene, polyvinyl chloride, polyurethane, epoxy resin, polyester, polycarbonate, polyoxymethylene, polystyrene, polyphenylene oxide, polyphenylene sulfide, polyimide, polysulfone and the like.

The suitable fully vulcanized powdery rubber used in the present invention can be the powdery rubber prepared by the process, which is disclosed in Chinese Patent Application No. 99125530.5 filed on December 3, 1999 by the present inventor. Said powdery rubber comprises at least one fully vulcanized powdery rubber selected from the group consisting of fully vulcanized powdery natural rubber, fully vulcanized powdery styrene-butadiene rubber, fully vulcanized powdery carboxylated

styrene-butadiene rubber, fully vulcanized powdery nitrile rubber, fully vulcanized powdery carboxylated nitrile rubber, fully vulcanized powdery polybutadiene rubber, fully vulcanized powdery chloroprene rubber, fully vulcanized powdery silicone rubber, fully vulcanized powdery acrylic rubber and the like. Said fully vulcanized powdery rubber has a gel content of at least 60% by weight, more preferably at least 75% by weight.

When preparing the present fully vulcanized thermoplastic elastomer, the fully vulcanized powdery rubber can be added in the form of dry cross-linked powder or wet cross-linked emulsion, deperding on processing requirement, when being blended with the plastic.

During preparation, blending temperature of the materials is that suitable for common plastic processing, which is determined by the melting temperature of the plastic matrix and should be selected within such a range where the plastic matrix is melt completely without decomposition. In addition, conventional processing aids and compatibilizer for plastic processing can be suitably added to the blended materials, if desired.

The rubber/plastic blending equipment used in the present invention is two roll mill, Banbury mixer, single-screw extruder or twin-screw extruder and the like.

Compared with the particle size of the rubber phase of the fully vulcanized thermoplastic elastomer obtained by conventional dynamic vulcanization, the particle size of the rubber phase of the present fully vulcanized thermoplastic elastomer is much smaller, which results in the great improvement of tensile strength and breaking elongation, good appearance and good processibility. The process of the present invention is simple, of low

equipment cost and controllable in operation, which meet the requirements for large-scale commercial production, due to the utilization of the conventional rubber/plastic blending equipment and common blending/extruding method.

The following specific examples will provide further illustrations of the present invention. These examples are not intended, however, to limit or restrict the scope of the invention as defined in the claims.

Figure 1 is the TEM micrograph of the sample obtained in Example 2.

Examples 1:

Fully vulcanized powdery styrene-butadiene rubber with an average particle size of about 0.1μ (which is prepared as follows: adding 3% trimethylolpropane triacrylate as cross-linking agent into the styrene-butadiene rubber latex, (Dingben-50, available from Latex Research Center of Lanzhou Petrochemical Co., Ltd, GanSu, China), based on the mass of dried styrene-butadiene rubber latex, and then vulcanizing the formulation with the irradiation dose of 2.5 Mrad, and drying it via spray drying method) and polypropylene (Designation 1300, available from Yanshan Petrochemical Co., Ltd, Beijing, China) are blended at a ratio of 70/30, then 0.5% of antioxidant Irganox 1010 was added. The obtained formulation is extruded and pelletized in a ZSK-25 model twin-screw extruder (WP company, Germany). The temperature of the individual sections of the extruder is set at 170℃, 190℃, 190℃, 190℃, 190℃ and 195℃ (die temperature), respectively. After preparing the standard sample bar of thus obtained fully vulcanized styrene-butadiene rubber/polypropylene thermoplastic elastomer pellets by injection mould method, the results of the analysis of the standard sample bar are listed in Table 1. The whiteness of the thermoplastic elastomer is 35.57 (according to GB2913-88), which enables to dye the articles made

therefrom to any desired colors.

Examples 2:

Fully vulcanized powdery styrene-butadiene rubber with an average particle size of about 0.1μ, as described in Example 1, and polystyrene (designation: 666D, available from Yanshan Petrochemical Co., Ltd, Beijing, China) are blended at a ratio of 70/30, then the obtained formulation is extruded and pelletized in a ZSK-25 model twin-screw extruder (WP Company, Germany). The temperature of the individual sections of the extruder is set at 170℃, 185℃, 185℃, 185℃, 185℃ and 190℃(die temperature), respectively. The pellets are injection-moulded into standard specimen bar for testing. The properties of the fully vulcanized styrene-butadiene rubber/polystyrene thermoplastic elastomer are listed in Table 1.

Example 3:

The procedure in Example 2 is repeated except that polystyrene is replaced with high-impact polystyrene (designation: 492J, available from Yanshan Petrochemical Co., Ltd, Beijing, China). The properties of the fully vulcanized styrene-butadiene rubber/high-impact polystyrene thermoplastic elastomer tested are listed in Table 1.

Example 4:

The procedure in Example 1 is repeated except that said polypropylene is replaced with polypropylene (designation: 1740, available from Yanshan Petrochemical Co., Ltd, Beijing, China). The properties of the fully vulcanized styrene-butadiene rubber/polypropylene thermoplastic elastomer tested are listed in Table 1.

Example 5:

Fully vulcanized powdery carboxylated styrene-butadiene rubber with an average particle size of about 0.15μ (which is prepared as follows: adding 3% isooctyl acrylate as cross-linking agent into carboxylated styrene-butadiene rubber latex XSBRL-54B1 (available from Yanshan Petrochemical Co., Ltd, Beijing, China) based on the mass of dried carboxylated styrene-butadiene rubber latex, and vulcanizing the formulation with the irradiation dose of 2.5Mrad, then drying it via spray drying method) and Nylon-6 (1013B, manufactured by UBE Industries, Ltd., Japan) are blended at a ratio of 75/25, then the obtained formulation is pelletized in a ZSK-25 model twin-screw extruder (WP Company, Germany). The temperature of the individual sections of the extruder is set at 210℃, 225℃, 225℃, 225℃, 230℃, and 225 ℃ (die temperature), respectively. The pellets are respectively compression-moulded and injection-moulded into standard specimen bars for testing. The properties of the fully vulcanized carboxylated styrene-butadiene rubber/Nylon-6 thermoplastic elastomer tested are listed in Table 1.

Example 6:

The procedure in Example 5 is repeated except that the blending ratio of fully vulcanized powdery carboxylated styrene-butadiene rubber to Nylon-6 is changed to 50/50. The properties of the fully vulcanized powdery carboxylated styrene-butadiene rubber/Nylon-6 thermoplastic elastomer tested are listed in Table 1.

Example 7:

Fully vulcanized powdery carboxylated styrene-butadiene rubber and Nylon-6 as used in Example 5 are blended at a ratio of 70/30, and then pelletized in a Brabender single screw extruder. The temperature of the individual sections of the extruder is set at 160℃,190℃,230℃,225℃,

respectively. The pellets are injection-moulded into standard specimen bar for testing. The properties of the fully vulcanized powdery carboxylated styrene-butadiene rubber/Nylon-6 thermoplastic elastomer tested are listed in Table 1.

Example 8:

Fully vulcanized powdery carboxylated styrene-butadiene rubber with an average particle size of about 0.15μ (which is prepared by the same procedure of Example 5 except that the irradiation dose is 10Mrad) and Nylon-6 (1013B, available from UBE Industries, Ltd., Japan) are blended at a ratio of 40/30, and the obtained formulation is pelletized in a Brabender single screw extruder. The temperature of the individual sections of the extruder is set at 160℃, 190℃, 230℃, and 225℃, respectively. Then, the obtained pellets and the above-mentioned carboxylated styrene-butadiene powdery rubber are blended at a ratio of 70/30, and the final ratio of powdery carboxylated styrene-butadiene rubber to Nylon-6 is 70/30. Then, the final formulation is pelletized in a ZSK-25 model twin-screw extruder (WP Company, Germany). The temperature of the individual sections of the extruder is set at 210℃, 225℃, 225℃, 225℃, 230℃ and 225℃(die themperature), respectively. The finally obtained pellets are injection-moulded into standard specimen bar for testing. The properties of the fully vulcanized carboxylated styrene-butadiene rubber/Nylon-6 thermoplastic elastomer tested are listed in Table 1.

Example 9:

Fully vulcanized powdery carboxylated nitrile rubber with an average particle size of about 0.05μ (which is prepared as follows: adding 3% trimethylol propane triacrylate as cross-linking agent into carboxylated nitrile rubber latex XNBRL (available from Latex Research Center of Lanzhou Petrochemical Co., Ltd GanSu, China) based on the mass of dried

carboxylated nitrile rubber latex, and vulcanizing the formulation with the irradiation dose of 10Mrad, then drying it via spray drying method) and Nylon-6 (1013B, available from UBE Industries, Ltd., Japan) are blended at a ratio of 70/30, and the obtained formulation is pelletized in a ZSK-25 model twin-screw extruder (WP Company, Germany). The temperature of the individual sections of the extruder is set at 210℃, 225℃, 225℃, 225℃, 230 ℃ and 225 ℃ (die temperature), respectively. The pellets are injection-moulded into standard specimen bar for testing. The properties of the fully vulcanized carboxylated nitrile rubber/Nylon-6 thermoplastic elastomer tested are listed in Table 1.

Example 10:

Fully vulcanized powdery natural rubber with an average particle size of about 0.5μ (which is prepared as follows: adding 5% trimethylol-propane triacrylate as cross-linking agent into the natural rubber latex (available from Beijing Latex Factory, China) based on the mass of dried natural rubber latex, and vulcanizing the formulation with the irradiation dose of 15Mrad, then drying it via spray drying method) and high density polyethylene (HDPE) resin (Designation: J-1, available from Beijing Second Auxiliaries Factory) are blended at a ratio of 70/30, and the obtained formulation is blended in a Brabender kneader for 2 minutes, with the temperature of oil bath for the kneader set at 160°C. The obtained sample is shaped into sheet by a two-roll mill (temperature: 160°C), and then tablettized to obtain the standard specimen for testing. The properties of the fully vulcanized natural rubber/polyethylene thermoplastic elastomer tested are listed in Table 1.

Table 1

| | | Tensile strength (MPa) | Elongation at break (%) | Tension set (%) | Tensile strength at 100% elongation (Mpa) | Shore Hardness |
|---|---|---|---|---|---|---|
| Example 1 | | 13.7 | 267 | 24 | 13.0 | 27(HD) |
| Example 2 | | 10.1 | 90 | 25 | - | 33(HD) |
| Example 3 | | 8.6 | 89 | 18 | - | 28(HD) |
| Example 4 | | 8.7 | 273 | 17 | 8.1 | 21(HD) 86(HA) |
| Example 5 | compressed specimen | 17.0 | 175 | 61 | 11.8 | 40(HD) |
| | Injection-moulded specimen | 16.4 | 216 | 101 | 10.5 | 40(HD) |
| Example 6 | compressed specimen | 29.4 | 188 | 96 | 23.2 | - |
| | Injection-moulded specimen | 27.6 | 200 | 129 | 22.5 | 56(HD) |
| Example 7 | | 19.2 | 134 | 38 | - | 39(HD) |
| Example 8 | | 19.8 | 167 | 70 | - | 46(HD) |
| Example 9 | | 19.1 | 126 | 28 | - | 40(HD) |
| ~~Example 10~~ | | ~~15.0~~ | ~~438~~ | ~~122~~ | | ~~86(HA)~~ |
| Test standard | | ASTM D412 | ASTM D412 | ASTM D412 | ASTM D 412 | ASTM D2240-95 |